Diffraction Patterns of Two Crystalline Forms of Oleic Acid*

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OF the considerable material published on the polymorphism of long chain compounds a substantial proportion has concerned straight chain saturated monocarboxylic acids. X-ray diffraction patterns for this homologous series show, by short spacing lines, very little evidence of polymorphism; principal spacings of 4.2 and 3.8 Å are the rule. Long spacing evidence, however, shows that four forms occur for certain members of the series with odd number of carbons, and three forms for certain members of the "even series." (1). Stearic acid, for example, can show three sets of spacings, according to its manner of crystallization (2). Transformations to forms stable at the respective melting points are so rapid that only a single melting point has been observed for any straight chain saturated monocarboxylic acid. Members of the "odd series," do show visual evidence of transformations (1).

While the evidence on unsaturated acids is much less extensive, it has been recognized for over thirty years that oleic acid is polymorphous (3) through observation of its two melting points, near 13° and 16°C. This was among the earlier observations, in point of number, of polymorphism in long chain compounds. It was apparently the very earliest relating to monocarboxylic acids. The two melting points of oleic acid have been confirmed several times, but as far as the author is aware, no x-ray diffraction data for the acid have been reported in the literature. Such data for the two generally recognized polymorphic forms have been obtained and are presented in this paper.

Experimental

Purified methyl oleate was obtained from olive oil methyl esters in a manner similar to that of Wheeler and Riemenschneider (4), which in turn is a modification of the method of Brown and Shinowara (5). Analyses were I.V. = 84.4, Linoleic (by Spectrophotometer) = 0.03%. Theory calls for I.V.= 85.5, Linoleic = 0.00%. The estimated composition is 98.5% methyl oleate, 1.5% saturated esters. Oleic acid was prepared from the ester and was characterized by its two melting points, which are shown in Table I in comparison with data for two highly reliable preparations.

TABLE I
Oleic Acid M. P.'s

Form	This preparation	S(6)	S.&W.(7)
Lower melting	13.3	13.36	13.4
Higher melting	16.2	16.25	16.2

No evidence for still higher melting forms (6, 8) was observed.

Unlike stearic acid, oleic acid supercools substantially, even below the lower melting point; it does not always crystallize immediately on chilling as low as 0°C. The lower melting form was prepared by chilling the melt in 1 mm. capillary tubes to —50°C. (then holding at 10°C.), and the higher melting form by holding the lower melting form 6 weeks at 10°C.

X-ray patterns were obtained in the manner previously described (9).

Diffraction data are shown in Table II.

TABLE II
X-Ray Diffraction Data for Oleic Acid

Lower Melting Form			Higher Melting Form		
Short Spacings					
d/n	*n*	*d*	*d/n*	*n*	*d*
4.64 M			4.65 V.S.		
4.43 W			4.37 M		
4.19 S			4.22 W		
4.01 W+			3.83 M		
3.93 W+			3.67 V.S.		
3.80 M			3.56 V.W.		
3.59 M			3.37 W		
3.53 V.W.			3.18 W—		
3.40 V.W.			2.95W		
3.31 V.W.			2.80 V.W.		
3.16 V.W.			2.69 W		
3.08 W			2.63 V.W.		
3.00 W—			2.49 V.V.W.		
2.48 V.W.			2.44 V.V.W.		
2.30 W			2.30 V.W.+		
2.26 W—			2.23 V.V.W.		
2.18 V.W.			2.19 V.W.		
2.11 V.W.					
Long Spacings					
40.13 V.S.	1	40.1	41.3 W	2	82.6
20.03 W	2	40.1			
13.49 S	3	40.5			
8.15 M	5	40.8	9.39 W	9	84.4
5.85 W+	7	41.0	8.65 W	10	86.5
			7.78 W	11	85.6
			6.86W—	12	82.4
			6.02 V.W.	14	84.4
			5.32 V.V.W.	16	85.2
Average 40.5 Å			Average 84.4 Å		

Discussion

Distinctive differences in the short spacing patterns of the two forms are readily noted. The lower melting form is characterized by a strongest line corresponding to 4.19 Å and other prominent lines corresponding to 3.80 and 3.59 Å. There is some resemblance to the patterns of stearic acid. The stable form pattern of oleic acid has two very strong lines corresponding to 4.65 and 3.67 Å. The prominent 4.65 Å spacing sets this form quite apart from any form thus far reported for long chain monocarboxylic acids.

It seems notable that azelaic acid in one of its two forms is one of a number of long chain compounds which also show prominent spacings of approximately 4.6 Å (10, 11). Azelaic is, of course, a dicarboxylic acid which is readily derivable from oleic acid. Some relation in crystalline structure between the oleic and azelaic acid forms is suggested.

Long spacing data for the two forms show differences as striking as do the short spacing data. In the case of the lower melting form the long spacing value of 40.5 Å and the strong intensity of the odd orders of the long spacing indicate a rather typical tilted double-chain-length structure with carboxyl groups head to head. The long spacing value falls between

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the "B" and "C" values of stearic acid which are 43.75 and 39.75 respectively (12).

The long spacing value of the higher melting form appears to be 84.4 Å. The possibility remains, however, that the true value is 42.2 Å since an apparent 9th order is the only odd order observed for 84.4 Å. The intensities of the long spacing lines, as a whole, are quite weak, and the distribution of intensity among the various long spacing orders is unusual. There is a complete absence or extreme weakness of orders between the 2nd and 9th; the common condition of strong intensity of odd orders, which was observed for the lower melting form, does not prevail. Whatever the crystal structure may be, it seems very likely that it deviates from the head to head arrangement usually observed for crystallized monocarboxylic acids.

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Summary

X-ray diffraction data are reported for the two polymorphic forms of oleic acid, melting respectively at approximately 13° and 16°C. The very striking differences observed in the patterns of the two forms point to profound differences in crystalline structure.

The lower melting form, with its main short spacing of 4.19 Å, its long spacing of 40.5 Å, and its relatively strong intensity for the odd orders of long spacing, suggests similarities in structure to the "B" and "C" forms of stearic acid.

On the other hand, the higher melting form is probably unique in crystal structure among the forms of long chain monocarboxylic acids for which diffraction data have thus far been reported. This form has main short spacings of 4.65 and 3.67 Å, a long spacing of 84.4 Å (possibly 42.2 Å), and a very irregular and unusual distribution of intensity among the various orders of long spacing.

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Abstracts

Oils and Fats

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INVESTIGATION OF THE SEED OILS OF SOME SUDAN CAESALPINIOIDEAE. D. N. Grindley (Sudan Med. Service, Khartoum). *J. Soc. Chem. Ind. 65,* 118-19 (1946). Analyses of seed oils of *Erythrophleon guineese, Parkinsonia aculeata, Cassia fistula, Tamarindus indica,* and *Cassia arereh* are given.

GRAIN STORAGE STUDIES. III. THE RELATION BETWEEN MOISTURE CONTENT, MOLD GROWTH, AND RESPIRATION OF SOYBEANS. M. Milner and W. F. Geddes (Minn. Agr. Exper. Sta., St. Paul). *Cereal Chem. 23,* 225-47 (1946). Relative humidity rather than actual moisture content of seeds determines their susceptibility to molding. It is concluded that the various "critical" moisture values for different seed species (*e.g.,* flaxseed 10.5%, wheat 14.5%) are those moisture contents which are in hygroscopic equilibrium with a common relative humidity of about 75% which, over moderate time intervals, is the minimal humidity required for the growth of the most xerophytic mold species which contaminates the seed.

SOLVENT EXTRACTION OF COTTONSEED AND PEANUT OIL. EFFECT OF HEAT ON COTTONSEED OIL MISCELLAS. H. L. E. Vix, E. F. Pollard, J. J. Spadaro, and E. A. Gastrock (So. Regional Res. Lab., New Orleans, La.). *Ind. Eng. Chem. 38,* 635-42 (1946). Heating of cottonseed oil miscellas at various temperatures and definite time periods under appropriate reduced pressures was carried out to determine the effect of heat on the resulting refined and bleached oils. Color fixation became objectionable between 150° and 180° F., and beyond 180° increased rapidly. Properly prepared solvent-extracted cottonseed oils from a prime lot of seed were successfully refined by slightly modified official A. O. C. S. refining methods which yielded oils of prime quality with low refining losses. Results have yielded necessary engineering information useful for design and operation of pilot plant equipment and for processing operations.

SODIUM CHLORITE IS SUCCESSFULLY USED FOR BLEACHING TALLOW. J. B. Tuttle (Theobald Industries, Inc., Kearny, N. J.), and E. R. Woodward. *Chem. & Met. Eng. 53,* No. 5, 114-15 (1946). Bleaching tallow with $NaClO_2$ is based on the production of ClO_2, a powerful oxidizing gas. Commercially, this is done by adding chlorite and either of 2 activating agents to the kettle.

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